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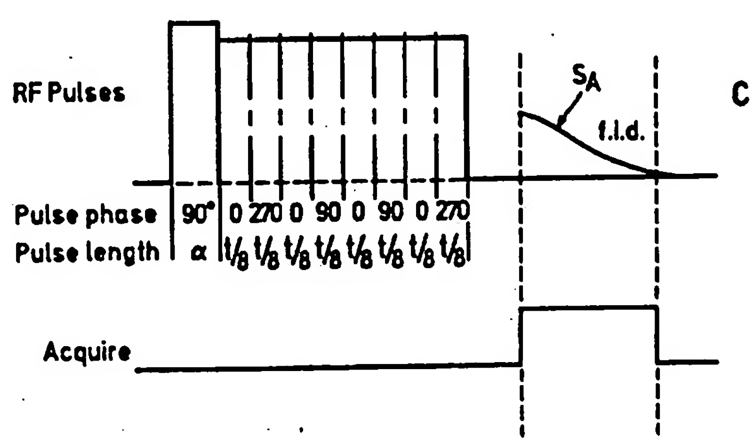

(57) Abstract

A method of nuclear quadrupole resonance testing a sample comprising a first type substance containing quadrupolar nuclei and a second type substance which may give rise to spurious signals which interfere with response signals from the quadrupolar nuclei, comprises applying a pulse sequence to the sample to excite nuclear quadrupole resonance, the pulse sequence comprising at least one pair of pulses; detecting response signals; and comparing, for the or each such pair, the respective response signals following the two member pulses of the pair; the pulse sequence being such that the respective spurious signals following the two member pulses can be at least partially cancelled by the comparison without the corresponding true quadrupole resonance signals being completely cancelled; and for the or each such pair, the two member pulses being of like phase.

METHOD OF AND APPARATUS FOR NUCLEAR QUADRUPOLE RESONANCE TESTING A SAMPLE, AND PULSE SEQUENCE FOR EXCITING NUCLEAR QUADRUPOLE RESONANCE

The present invention relates to a method of and apparatus for nuclear quadrupole resonance testing a sample, as well as to a pulse sequence for exciting nuclear quadrupole resonance (NQR). The invention has particular application to the detection of the presence of a given substance in a sample. The sample may contain or be suspected of containing nuclei of integral or half-integral spin quantum number ($I \geq \frac{1}{2}$).

NQR testing is used for detecting the presence or disposition of specific substances. It depends on the energy levels of quadrupolar nuclei, which have a spin quantum number I greater than ½, of which ^{14}N is an example ($I = 1$). ^{14}N nuclei are present in a wide range of substances, including animal tissue, bone, food stuffs, explosives and drugs. One particular use of the technique of the present invention is in the detection of the presence of substances such as explosives or narcotics. The detection may be of baggage at airports, or of explosives or drugs concealed on the person or buried underground or elsewhere.

In conventional Nuclear Quadrupole Resonance testing a sample is placed within or near to a radio-frequency (r.f) coil and is irradiated with pulses or sequences of pulses of electro-magnetic radiation having a frequency which is at or very close to a resonance frequency of the quadrupolar nuclei in a substance which is to be detected. If the substance is present, the irradiant energy will generate a precessing magnetization which can induce voltage signals in a coil surrounding the sample at the resonance frequency or frequencies and which can hence be detected as a free induction decay (f.i.d.) during a decay period after each pulse or as an echo after two or more pulses. These signals decay at a rate which depends on the time constants T_2^* for the f.i.d., T_2 and T_{2e} for the echo amplitude as a function of pulse separation, and T_1 for the recovery of the original signal after the conclusion of the pulse or pulse sequence.

As described in United States Patent No. 5,365,171 (Buess et al.), spurious interfering signals (also termed "ringing") may sometimes arise from a sample during NQR tests which are not associated directly with or due to the nuclear resonance.

echo, depends on the relative phases of the two preceding pulses, unlike that of the interfering signal, which is determined almost entirely by that of the immediately preceding pulse.

This distinction has been exploited in the afore-mentioned United States patent in an attempt to remove the interfering signal from an NQR response signal. The proposed solution involves the continuous use of phase alternating excitation pulses and the addition or subtraction of the response signals from the various pulses, which has the effect of reducing the spurious signals.

Whilst the afore-mentioned United States patent also describes a solution to the problem of spurious ringing, it has been found in practice that this solution may lack versatility, in that it is restricted to the use of one particular phase alternating pulse sequence. This sequence may not be the most favourable in all circumstances.

Indeed, and in particular, the technique proposed in this United States patent has been found to have the limitation that the separation between adjacent pulses in the phase-alternated sequence which is employed must be longer than the decay time of the interfering signal. If, contrary to the teachings of this patent, the interfering signal generated in response to a first pulse were to persist through to a subsequent pulse of different phase and be detected subsequent to that pulse, a portion of the interfering signal, rather than being subtracted out from the response signal, would actually be added to the signal. This imposes very severe restraints on the sensitivity of the technique.

Also, the technique proposed in the United States patent has been found not to be capable of completely cancelling all spurious instrumental artefacts, such as errors in the phases of the excitation pulses.

The present invention seeks to solve these and other problems.

According to the present invention, there is provided a method of nuclear quadrupole resonance testing a sample comprising a first type substance containing quadrupolar nuclei and a second type substance which may give rise to spurious signals which interfere with response signals from the quadrupolar nuclei, comprising:

applying a pulse sequence to the sample to excite nuclear quadrupole resonance, the pulse sequence comprising at least one pair of pulses;

detecting response signals; and

comparing, for the or each such pair, the respective response signals following the two member pulses of the pair,

as phase errors in the individual excitation pulses.

A phase cycling technique commonly termed "Cyclops" is known in the NMR field. However, this technique is not closely related to the present technique; in particular, it would not be capable of removing interfering signals.

In one preferred variant of the phase cycling feature, if first and second individual pulse sequences are provided, and if the first and second individual pulse sequences together form a first pair of such sequences, an additional, second pair of individual pulse sequences is provided, and the phases of the respective next pulses following each initial pulse in the second pair differ from the phases of the corresponding pulses in the first pair. The phases of the two respective initial pulses of the second pair of individual pulse sequences may be in quadrature with the phases of the corresponding pulses in the first pair. Apart from a different set of phases for each pair, the corresponding pulse sequences in the different pairs are preferably identical.

The invention provides variants of the phase cycling technique in which either two or four pairs of individual pulse sequences are provided, with appropriate cycling of the phases of the various pulses through the 360° range. More generally, if n pairs of individual pulse sequences are provided, preferably the respective next pulses following the initial pulse in the corresponding individual sequences in each pair have phases which are equally distributed through a 360° range. Preferably, n is 2 or 4, but it may take other values, such as 6 or 8.

Another important preferred feature of the invention is that, for the or each such pair of pulses, the times between the respective pulse preceding each member pulse of the pair and the detection in the detection step of the respective response signal following each member pulse of the pair are sufficient for the spurious signals to decay to below 50% (preferably below 30, 20 or 10%) of their initial value by the end of said times. Preferably also, for each individual pulse sequence (if provided) there is a delay of a predetermined duration between the end of the initial pulse and the beginning of the detection for that sequence.

By judicious choice of the time or delay duration, this can afford a convenient additional technique for removing or reducing the spurious signal. As demonstrated later, introduction of such a time or delay need not interfere with the proper functioning of the remainder of the pulse sequence.

The time or delay is preferably sufficient to, more preferably only just

The initial pulses may be thought of as preparation pulses (following which signals are not usually acquired), typically having different characteristics from the remaining pulses in the sequence. For example, and perhaps most importantly, each initial pulse preferably has a different phase from the or any further pulse which follows it in the same individual sequence. This has been found to be an important feature in obtaining sensitive test results. It is particularly preferred that the phase of the initial pulse is in quadrature with the phase of the next pulse in the sequence, since this has been found to be the optimal phase relationship between the two pulses.

More usually, neither of the initial pulses have the same phase as the or any further pulse in either individual sequence. However, this feature may not always be necessary. For instance, a phase-alternated sequence as suggested in United States Patent No. 5,365,171 could be used in combination with an initial preparatory pulse of different phase, for both the first and second individual pulse sequences. One advantage this would have over the U.S. patent would be more or less complete removal of instrumental artefacts.

A further preferred feature is that, if, as may be advantageous, a plurality of further pulses are provided in each individual sequence, each such further pulse in the same sequence has the same phase. This is an important feature for two reasons. Firstly, it can render the invention simpler to put into practice. Secondly, and perhaps more significantly, it can enable the accumulation of signals from each of the further pulses in a way which can reinforce the nuclear resonance signal whilst eliminating the interfering signal.

In the preferred embodiments, the two initial pulses differ in phase by 180°, whilst all the further pulses have a phase which is in quadrature with that of the initial pulses.

Preferably, the pulse sequence includes (at least) a first pulse and a second pulse, the second pulse at least partially locking the magnetization (of the quadrupolar nuclei) generated by the first pulse. Such a sequence may be termed a "spin locking" sequence, with the magnetization being locked for a time longer than would be achievable with the equivalent single pulse. Locking can be achieved by keeping the B_1 field parallel to the magnetization, which can require that the second pulse differs in phase from the first pulse by between roughly 45 and 180°, preferably 70 and 135°, and more preferably 80 and 110°. The spin locking sequence has the important advantage of being able to lock the magnetization beyond (even beyond 2, 3 or 5

compensated.

In the phase split pulses variant, preferably the second pulse includes a third element having a phase different from said two phase alternated elements. The third element can enhance sensitivity by providing a further lock on the magnetization. The phase of the third element is preferably intermediate the phases of the first and second elements, and is typically 90° separated from both.

In a further variant of the first preferred embodiment ("stacked pulses") the length of the second pulse (of the pulse sequence) may in certain circumstances be less than, preferably no more than 75% of, more preferably no more than 50% of, the length of the first pulse. This can afford the most important advantage of generating magnetization greater than (typically at least 5, 20 or 50 % greater than) that predicted to be available by the appropriate Bessel function. For a spin-1 system the Bessel function predicts that 44% of the total magnetization is available using a single pulse, but using stacked pulses up to 62% or even more may be available.

Preferably, the phase of the second pulse is in quadrature with that of the first pulse. This can optimise the performance of the pulse sequence.

Preferably also, the pulse sequence includes a third pulse at least partially locking the magnetization of the first and second pulses, and preferably being of phase intermediate that of the first and second pulses. This can further assist in locking the magnetization.

Preferably, at least one of the first and second pulses comprises a plurality of elements of different phase (or frequency), so that different spectral profiles can be provided.

Preferably again, the phases of the first and second pulses are arranged so as to provide together excitation peaks at at least two different frequencies. This feature could, for example, be used to excite virtually simultaneously different resonance frequencies in the NQR substance, as also taught in United Kingdom Patent No. 2,286,248 (to British Technology Group Limited).

In a second preferred embodiment, echo signals are generated. Broadly, the signal to noise ratio achievable with the second embodiment will be worse than that achievable with the first embodiment for substances for which $T_{1\rho}$ is longer than T_2, but attenuation of spurious signals will be better.

In a first variant of the second embodiment, which has been found to operate successfully, the pulse sequence comprises at least one pulsed spin locking pulse

the pulses. This can be achieved, for example, by suitable shaping of the pulse.

Preferably also, the true quadrupole resonance signal is distinguished from the spurious signal in dependence on its (time) gradient, curvature or shape, perhaps in dependence upon whether the true and spurious signals have gradients of opposite sign. This feature arises from the realization made pursuant to the present invention that as the interfering signal decays the true NQR echo signal rises, and that this can be used to distinguish between the two signals. The feature may be put into effect by a filter using a rising exponential function, which has been found experimentally to increase the differentiation of the NQR signal relative to that of the spurious signal by at least 50%.

It is advantageous to incorporate a delay in signal acquisition into the pulse sequence, as suggested above. In the second embodiment this can be achieved in at least two different ways.

In one preferred variant of the second embodiment, the time τ (which is the separation between the initial pulse and the next pulse in the sequence) is set greater than a predetermined duration.

In an alternative preferred variant (suitable particularly for Pulsed Spin Locking), the time τ is set at a relatively short value, but signals from the echoes are only detected after the first few (say, two, five, ten or greater) pulses of the sequence.

The advantage of the latter, alternative variant over the former is that it can yield a better signal to noise ratio.

Also in connection with the second preferred embodiment, it has been discovered that the value of the pulse separation τ is advantageously as small as possible. Hence, it is preferred that the separation between each initial pulse and the next pulse in the sequence is less than once or twice the value of T_2^* of the nucleus whose nuclear resonance is being excited; it may possibly be preferred that this is less than 0.5, 0.3 or even 0.1 times T_2^*.

A third preferred embodiment of the present invention essentially combines the features of the first and second preferred embodiments.

The invention is preferably performed in the absence of an applied magnetic field.

In a closely related aspect of the present invention, there is provided apparatus for nuclear quadrupole resonance testing a sample comprising a first type substance containing quadrupolar nuclei and a second type substance which may give rise to

Figure 6 is a plot similar to that of Figure 5, but showing three different plots corresponding to three different pulse lengths for an initial preparatory pulse, P1;

Figure 7 is a plot of signal intensity versus the length of the initial pulse, P1, illustrating a comparison between two different types of pulse;

Figure 8 is a plot of signal intensity versus time derived using a second variant of the first embodiment;

Figure 9 is a plot of signal intensity versus frequency derived using a third variant of the first embodiment, compared with a similar plot derived using a single excitation pulse;

Figure 10 is a plot of signal intensity versus frequency derived using first and fourth variants of the first embodiment;

Figure 11 is a pulse timing diagram for use with a second preferred embodiment of the present invention;

Figure 12 is a plot of real and imaginary signal intensities versus time derived using a first variant of the second embodiment of the invention;

Figure 13 is a plot of signal intensity versus pulse separation (τ) derived using the first variant;

Figure 14 is a plot of signal intensity versus frequency derived using the first variant, at a first value of flip angle (119°_{actual});

Figure 15 is the comparable plot at a second value of flip angle (33°_{actual});

Figure 16 is a plot of signal intensity versus time derived using the first variant;

Figure 17 is a plot of signal intensity versus time derived using a second variant of the second embodiment;

Figure 18 is a plot of signal intensity versus time derived using the second and a third variant of the second embodiment; and

Figure 19 is a similar plot to that of Figure 18 to a different scale of signal intensity.

APPARATUS

Referring first to Figure 1, apparatus for NQR testing includes a radio-frequency source 11 connected via a phase/amplitude control 10 and a gate 12 to an r.f. power amplifier 13. The output of the latter is connected to an r.f. probe 14 which contains one or more r.f. coils disposed about or adjacent the sample to be tested (not

Shown diagrammatically in Figure 1 and designated as 27 is some means, such as a conveyor belt, for transporting a succession of samples to a region adjacent the r.f. probe 14. The computer 16 is arranged to time the application of the excitation pulses substantially simultaneously with the arrival of a particular sample adjacent the probe. In alternative embodiments, instead of the sample being carried on a conveyor belt, it may actually be a person, and the r.f. probe may be in the form of a walk-through gateway or a hand-held wand.

Although the apparatus described above would usually employ rectangular pulses, other pulse shapes may be employed. Furthermore although usually the radio-frequency probe would utilise a single coil for both transmission and reception of signals, any appropriate number of coils may be used, and different coils can be used for transmission and reception. Also, the apparatus would usually operate in the absence of any applied magnetic field.

PRINCIPLE OF PHASE EQUIVALENCE, AND SPURIOUS SIGNAL CANCELLATION

In a sequence of r.f. pulses, of any amplitude, length and shape, which has been designed to distinguish between genuine NQR signals and spurious interference from the sample by means of phase cycling, it is important to compare and manipulate responses generated by r.f. pulses which as far as possible have the same relative phase. In other words, "like" is compared with "like"; this principle is termed herein the principle of "phase equivalence".

It is also advisable that these pulses be identical in other respects such as amplitude, frequency, shape and length, or at least that the consequences of any such differences can be allowed for, but the principle of equivalent phases is the most important. Satisfying this principle can ensure that any spurious response, the phase of which differs from that of the exciting pulse by an unknown amount, can be annulled by means of a suitable phase cycle.

The pulse sequences described pursuant to the present invention can satisfy the principle of phase equivalence.

The discovery of the principle of phase equivalence pursuant to the present invention is predicated on the following theoretical and experimental findings.

The response of many materials to an r.f. pulse may depend on the precise phase of that pulse, not merely its amplitude. The response may also depend on the

equivalent pulses being compared to be different. Preferably the phases differ by 180°, but lesser phase differences could also produce satisfactory results.

In order that the comparison yields meaningful results, it is preferred that the first and second individual pulse sequences (if provided) generate respective nuclear response signals of the same magnitude but of differing phase. This is achieved in the preferred embodiments by having the same number of pulses in both sequences, by comparable pulses in each sequence having the same phase, and by comparable pulses in each sequence generating the same flip angle. If, aside from the initial pulse, more than one further pulse is provided per individual sequence, such pulses may each be separated by the same pulse separation; that separation may be larger than the separation between each initial pulse and the next pulse in the sequence.

Three different preferred embodiments of the present invention, all adhering to the above principles, are now described for use with the testing apparatus described above.

FIRST EMBODIMENT - SPIN LOCKING SEQUENCES

In a first preferred embodiment of the invention, in brief interfering signals are removed from the free induction decay following two radio-frequency pulses comprising a "spin locking" (SL) type sequence.

The basic technique is to use an initial preparation pulse of flip angle 90° and phase 0° (termed a "$90°_{0°}$" pulse) to rotate the magnetization into parallelism with (say) the Oy axis of the rotating frame (B_0 lies along Oz and B_1 along Ox). This pulse is then immediately followed by the so-called spin locking pulse of variable length and a phase shifted by 90° with respect to the first. Hence the combination of the two pulses can be written in the form $(90°)_{0°} - t_{90°}$, where "t" represents the adjustable length of the second pulse. The combination of the two pulses is sometimes known as a sandwich or composite pulse. However, herein, throughout, the combination is regarded as two distinct pulses.

In the spin locking phase of the cycle, the magnetization is parallel to the r.f. field, and is observed to decay with a time constant $T_{1\rho}$, the spin-lattice relaxation time in the rotating frame. In contrast, after a single 90° pulse, the magnetization would decay with a time constant T_2 or T_2^*. In many substances $T_{1\rho}$ is much closer to T_1 than T_2 or T_2^*; since in solids $T_1 >> T_2$, spin locking can conserve the magnetization for a much longer period of time.

preparatory pulse has been shifted by 180°. Hence the sequence is $\alpha_{180°}-t_{90°}$, which generates the signal

$$S_B = -Q + I$$

Subtraction of S_A and S_B then removes I and sums Q.

Usually a large number of A and B sequences would be applied to the sample, to improve the signal to noise ratio, with the results from the two sequences either being separately accumulated or being processed immediately. The sequences may for instance be performed in the order ABABABAB..., or in the order AAA... BBB.... Usually the same number of A and B sequences would be performed, with the intent that the comparison between the A and B sequences is as close as possible.

Second variant of the first embodiment – full phase cycling

In a more complex but more effective version of the first preferred embodiment, a complete phase cycle is utilised in which all possible combinations of the phases of the two pulses in the pulse sequence are used, subject to the condition that the first pulse differs in phase from the second by 90°. Hence one possible set of phase cycled sequences, using four pairs of individual sequences, is as follows:

Sequence type	Phase of first pulse (P1)	Phase of second pulse (P2)	Receiver Phase	Real Channel	Imaginary Channel
A	0°	90°	90°	+Y	−X
B	180°	90°	270°	−Y	+X
A	90°	180°	0°	+X	+Y
B	270°	180°	180°	−X	−Y
A	180°	270°	270°	−Y	+X
B	0°	270°	90°	+Y	−X
A	90°	0°	0°	+X	+Y
B	270°	0°	180°	−X	−Y

It is to be noted that the shift in the receiver phase between the A and the B sequences is 180°, so that subtraction of the B sequence signals from the A sequence signals can be effected. It is also to be noted that the receiver phase is not necessarily

Third variant of the first embodiment - phase split pulses

Variations in temperature or other such environmental parameters may affect the resonance frequency of the nuclei under investigation. Whilst the pulse sequence shown in Figures 2(a) can operate successfully at off-resonant conditions, over a limited bandwidth, an alternative version of the pulse sequence is capable of considerably better off-resonant performance. This sequence, involving the use of what are herein termed "phase split pulses", is now described with reference to Figures 2(b). The sequence is capable of increasing the NQR signal.

The background to the alternative pulse sequence is as follows. During the spin locking phase of sequence A shown in Figures 2(a), at off-resonant conditions the magnetization generated by the first pulse processes (or nutates) about the resultant of ω_1 and $\Delta\omega_Q$ (where $\Delta\omega_Q$ is the off-resonant frequency shift), so that the magnetization vector dephases. It has been found pursuant to the present invention that, to take into account the difficult conditions in the rotating frame and to improve the sensitivity of the tests off-resonance, it may be advantageous to regenerate the initial state. This, it has been found, can be achieved by reversing the direction of B_1 (or (ω_1/γ)) by means of a 180° phase shift in the spin locking pulse; if this phase reversal is performed exactly half-way through the spin locking pulse, the reversal of the spin nutation about the resultant of ω_1 and $\Delta\omega_Q$ regenerates the original signal (that is, refocusses the magnetization) at the end of the spin locking sequence (apart from any change due to relaxation which, it is believed, would be relatively minor).

Figures 2(b) illustrate this phase reversal technique. The spin locking pulses shown in Figures 2(a) (of length t and phase 90°) are replaced in Figures 2(b) by spin locking pulses split into equal portions of length t/2 and of phase respectively 90° and 270°. In similar fashion to that described previously, subtraction of the free induction decays following cycles A and B respectively removes the spurious ring-down following the end of the spin locking pulse. Again as described previously, the free induction decay following the initial preparation pulse is effectively removed by allowing the spin locking pulse to run for sufficient time for the spurious interfering signals to decay to zero. A pulse length for the spin locking pulse of between 1 and 3 or 4 ms has been found to be effective for the 3.41 MHz transition in RDX.

In order to eliminate spurious signals more effectively, a complete phase cycle can be performed in a fashion analogous to that already described above. This may be, for example, either the two or the four pair cycle mentioned previously.

attempt to lock both these components for at least part of the spin locking period. A phase shift of 180° is then added to refocus in part those components which have moved seriously away from parallelism with B_1 during the first three segments.

The resultant response signal obtained by using the A and B sequences of Figures 2(c) is asymmetric in the frequency domain, since phase changes are equivalent to changes in frequency. Therefore in an enhancement of the second sub-variant, the A and B sequences are combined with "mirror image" C and D sequences, as shown in Figures 2(d). The summed responses of the sequences A to D, implemented sequentially, can provide a performance which is symmetrical about the excitation carrier frequency and which has relatively broad bandwidth.

Similar improvements in excitation bandwidth could be obtained by applying discrete changes in frequency between individual pulses. Furthermore, a combination of both phase shifts and frequency changes could produce an even better performance in that the changes in carrier frequency can be made to compensate for the changes in phase, an effect of some importance when long r.f. pulses of narrow bandwidth are necessary; this is explained in detail below in relation to the fourth variant. Also, further improvements could be obtained by using a full phase cycle, as described in relation to the second variant of the first embodiment.

<u>Fourth variant of the first embodiment – stacked pulses</u>

Another variant of the first embodiment is to combine two, three or more pulses of different phases and/or different widths, usually in the initial preparatory pulse. Such a combination of pulses is referred to as "stacked" pulses. Stacked pulses are also used in the second embodiment of the invention (described later); in this latter case they are used as stand-alone pulses, and are spin locking pulse sequences in their own right, although the lock may not be maintained particularly long.

In general terms, stacked pulses are particularly applicable when there is a restriction on the flip angle which can be generated by individual pulses, for example, when only low values of the B_1 field must be used. Hence, as an example, only 30° instead of the optimum value for spin-1 nuclei of 119° may be available.

A typical stacked pulse consists of several (say <u>n</u>) usually contiguous pairs of low flip angle pulses P1A and P1B, with a number of phase shifts, say of 90°, as for example $(P1A_{0°}-P1B_{90°})_n$, to effect the locking (n being greater than or equal to 1 and typically being 2, 3, 4, or even more). Such a pulse can function almost as well as

(say greater than 45°) greater than the phase of the preceding pulse.

An advantage of stacked pulses as described is that they can not only provide effective spin locking but also they can actually enhance the signal to noise ratio.

If the individual pulse lengths are seriously limited, it may be an advantage to use longer stacked sequences. For example, in a particular experimental set-up, with the sequence (P1AP1B), a pulse length of 10 μs, n = 2 gives the optimum response, whereas with a pulse length of 5 μs, n = 5 is required.

In the present context of spin locking pulses, a sequence of stacked pulses replaces the initial preparatory pulse, there being available all the previously discussed possibilities for use in the spin locking pulse. Phase cycling is then achieved by cycling the phases of the stacked pulses in the same way as for the basic spin locking pulse sequence (see the first and second variants of the first embodiment).

The following table shows two such suitable fully phase cycled sequences, the sequential combination of which yields a response which is reasonably symmetrical about the centre frequency. In the table, each pair of A and B pulses is repeated n number of times.

Sequence type	Phase of first part of stacked pulse (P1A)	Phase of second part of stacked pulse (P1B)	Phase of second pulse (P2)	Receiver Phase
A	90°	0°	0°	0°
B	180°	270°	270°	270°
A	270°	180°	180°	180°
B	0°	90°	90°	90°
A	270°	0°	0°	180°
B	0°	270°	270°	90°
A	90°	180°	180°	0°
B	180°	90°	90°	270°

General considerations for the first preferred embodiment

The important conditions to be advantageously maintained in the phase cycling technique of the first embodiment are firstly that, as regards all P2-type pulses, like is subtracted from like. That is, for example in the second of the four tables above (given in the section which describes the second variant of the first embodiment), the two 90° P2 free induction decay signals exactly cancel, as do the two 270° signals. Pulse and phase imperfections therefore cancel.

Secondly, the receiver phases are adjusted to allow appropriate subtraction of the interfering signals and free induction decay response signals.

Thirdly, the respective P2 type pulses in each A and B pair of individual sequences have phases which are preferably equally distributed through the 360° phase variation range.

Fourthly and finally, for each pair the P1 type pulses have phases which preferably are in quadrature with the phases of the P2 type pulses.

Various other conditions are also preferably fulfilled if any of the variants of the first embodiment of the present invention are to function satisfactorily. These are as follows.

Firstly, one particular condition is that the pulse length of the second, spin locking pulse, t, is sufficiently long to translate the NQR signal completely away from any interfering signal generated by the first, initial pulse, since this interfering signal is not removed by the phase shifting. Expressed somewhat differently, the pulse length of the next pulse following each initial pulse is preferably sufficiently long that any interfering signal generated in response to the initial pulse does not persist to any substantial extent beyond the end of that further pulse. This condition is now discussed in more detail.

It has been discovered that the interfering signals referred to above tend to decay fairly rapidly after an r.f. pulse, usually within, say, 350, 500, 750, 1000 or 1500 μs of the end of the pulse. Thus, provided the pulse length of the second pulse is chosen to be significantly more than the decay time of these signals, useful response data can be derived subsequent to the second pulse notwithstanding any interfering signal following the first. A pulse length equal to or greater than 200, 400, 500, 600, 700, 1000 or 1500 μs has been found empirically to be satisfactory in most circumstances. To make efficient use of the available test time, the length is preferably less than 3, 2, 1.5, 1 or even 0.7 ms. A sufficient decay for the response

to the sample, with the length of the initial pulse, P1 = 20 μs, and the spin locking pulse, P2, being of variable length. The four pair phase cycling sequence shown in the relevant table above was employed. The respective signal intensities following the second pulse, P2, were determined for 100 different values of the length of the second pulse. These 100 signal intensities have been plotted in Figure 3.

As can be seen from Figure 3, the signal intensity is almost constant out to 60 μs, then drops quite rapidly by about 20%, possibly when the length of P2 corresponds closely to a flip angle of $254°_{actual}$ (the value of the flip angle of a single pulse to produce the zero signal intensity for that pulse). It is to be noted that, although the units of the signal intensity are arbitrary, the plot does not extend down to the origin (which is zero).

Figure 4 shows a similar plot to that of Figure 3, but this time in the presence of nickel-plated screws, which are known to cause substantial interfering signals. The plot of Figure 4 has also been extended out to very much longer spin locking times. The full phase cycling sequence referred to above was again employed. It will be apparent that an NQR signal can be seen out to 2 ms, with some loss, and even out to 12 ms, but with significantly more loss. The presence of the screws considerably reduced the Q factor of the r.f. probe, and hence the signal to noise ratio of the response signals. Nevertheless, it has been ascertained that the interfering signals were substantially completely removed from the response signal. The interfering signals would have given rise to signals in the region of five to ten times as intense as the true NQR responses shown in Figure 4.

In a further experiment similar to that described in relation to Figure 4 (but not illustrated herein), no phase cycling was employed; in other words, only A-type pulse sequences were employed. In this experiment the NQR response was completely obscured by the interfering signals generated from the screws.

The plot of Figure 5, which is similar to that of Figure 3, but shows a different range of the length of the spin locking pulse, P2, has been used to provide an estimate of the NQR spin locking time, $T_{1\rho}$, at room temperature for the 3.42 MHz line of RDX with B_1 = 1.6 mT (noting that $T_{1\rho}$ may vary with B_1). The experimental data points are illustrated by the open circles, whilst the line shown is the best fit of an equation of the form

$$y = a.\exp(-x/b)$$

for lengths of the second P2 pulse longer than t = 3 ms. A least squares fit yields a

as successfully at off-resonant conditions over a limited bandwidth, especially where the version of the pulse sequence shown in Figures 2(b), (c) or (d) is employed.

Referring now to Figure 9, again using as a sample the explosive RDX at 3.41 MHz, there is shown by the triangular symbols the results of summing the responses to the phase split pulse sequences shown in Figures 2(c) and 2(d) and described as the third variant of the first embodiment, and then dividing this result by two, whilst stepping the excitation carrier frequency through 0.1 kHz increments. The preparatory pulse was of length 240 μs, whilst each of the eight phase split pulses were of length 275 μs, making a total pulse sequence length of nearly 2.5 ms. By the circular symbols is shown the results of a similar single pulse of length 240 μs, again stepping the carrier frequency through 0.1 kHz increments. It will be seen that the signal intensity for the phase split pulse sequences is at least 70 % of that for the single pulse, whilst the bandwidth of 3.5 kHz is roughly similar. This bandwidth represents a temperature variation of 38°C, demonstrating the good off resonance properties of the split pulse sequence.

Referring now to Figure 10, again using as a sample the explosive RDX at 3.41 MHz, there are shown the results of using stacked pulses (described as the fourth variant of the first embodiment), by comparison with the basic spin locking sequence described as the first variant. In all four cases illustrated in Figure 10 the spin lock was of the same duration (1 ms). As would be expected, the best results, both in terms of peak response and bandwidth, are obtained with a stacked pulse having $t_B = t_A/2$ (= 250 μs) and n = 3 (see the upright triangular symbols). The second best results are obtained with a stacked pulse having $t_B = t_A$ (= 250 μs) (see the circular symbols). The square data points were obtained with the basic spin locking sequence with the pulse length of the preparatory pulse equal to 250 μs. The inverted triangle data points were obtained with the basic spin locking sequence with the pulse length of the preparatory pulse equal to 125 μs.

SECOND EMBODIMENT - MULTIPLE PULSE ECHO TECHNIQUES

In a second preferred embodiment of the invention, in brief the interfering signals are removed by means of multiple pulse echo techniques.

With the second embodiment, the same principle of phase equivalence as was described above is used to remove spurious interfering signals from NQR echoes. Also the principle of reversing the phase of the initial, preparation pulse from

$$\alpha_{180°}-\tau-\alpha_{90°}-(-2\tau-\alpha_{90°}-)_n$$

where the time τ is the separation between the initial pulse and the next pulse in the sequence, and the time 2τ is termed the "pulse repetition time" for the remaining pulses.

It is noted that a PSL sequence uses the spin locking technique referred to previously.

As shown in the figure, acquisition of the response signal takes place between each of the $\alpha_{90°}$ pulses, but not directly after the initial (P1) $\alpha_{0°}$ or $\alpha_{180°}$ preparation pulses. In fact, acquisition is delayed somewhat even after the second (P2) pulses, to take account of instrumental ring down. In the sequences, n may take any appropriate value (including 1 or even 0 if only a short echo sequence is desired).

The two sequences are subtracted one from the other in a phase shifting technique analogous to that described above, to yield an echo response signal substantially free from interfering signals or indeed free induction decay signals.

<u>Second variant of the second embodiment – Steady State Free Precession pulse sequence</u>

In the second variant of the second embodiment of the present invention a number of Steady State Free Precession echo generating pulse sequences are disclosed; not all of these sequences use initial preparatory pulses, but they all still comply with the principle of phase equivalence.

In the first and simplest (non-spin locking) pulse sequence, a four pulse multiple pulse sequence with 180° phase shifts is employed:

$$\{\overset{A}{\alpha_{0°}}-\tau-\overset{B}{\alpha_{0°}}-\tau-\overset{C}{\alpha_{180°}}-\tau-\overset{D}{\alpha_{180°}}-\tau-\}_n$$

where n represents a repetition of the sequence and the angles shown are phases. The signals are combined as (A – B – C + D). This sequence fulfils the principle of phase equivalence in that only like phases are subtracted from one another. Spurious signal cancellation is, as usual, effected by the respective pulses immediately preceding the members of the particular pairs of pulses being compared (A and B, C and D) being of opposite phase.

Phase cycling can be achieved by employing a second sequence in which the 0° phases of the first sequence are replaced by 90° phases, and the 180° phases by 270° phases.

$$\{\alpha_{0°}-\tau-\alpha_{0°}-\tau_1-\alpha_{90°}-\tau_2-\alpha_{90°}-\tau_1-\alpha_{180°}-\tau_2-\alpha_{180°}-\tau_1-\alpha_{270°}-\tau_2-\alpha_{270°}-\}_n$$

which also functions well with $\tau_2 = 2\tau_1$. This sub-variant can enhance signal to noise ratio.

In a second sub-variant of the third variant, a specific sequence of the form:

$$\{\alpha_{90°}-\tau-\alpha_{0°}-2\tau-\alpha_{180°}-\tau-\alpha_{270°}\}\text{Acquire}$$

combined with:

$$\{\alpha_{0°}-\tau-\alpha_{180°}-2\tau-\alpha_{90°}-\tau-\alpha_{270°}\}\text{Acquire}$$

also functions well. It has particular benefits at low B_1 field, under which condition it can enhance magnetization and hence signal.

In a third sub-variant, the basic eight pulse sequence with 90° phase shifts is collapsed into a pair of individual composite spin locking stacked pulse sequences (see the first embodiment), for example:

$$\{\alpha_{0°}-\alpha_{90°}-\alpha_{180°}-\alpha_{270°}\}_n$$

$$\{\alpha_{180°}-\alpha_{90°}-\alpha_{0°}-\alpha_{270°}\}_n$$

The first pulse in each individual sequence effectively acts as a preparatory pulse, the second to effect some spin locking, the third to effect phase reversal, and the final pulse to effect spin locking. The individual sequence may generate an echo as well as a free induction decay.

The third sub-variant may be used either by itself or as part of another sequence. Each individual stacked pulse sequence could for example form a single pulse in the eight pulse sequence described above.

The third sub-variant has a good overall performance especially at higher B_1 field provided that the spin-locking time $T_{1\rho}$ is longer than the overall pulse length; because this is a "long" pulse, its excitation bandwidth can be narrow.

In a fourth sub-variant, each pulse of the basic eight pulse sequence may be replaced by a two (or more) pulse stacked-type spin locking sequence, for example

Sequence (NPAPS). It is claimed that the combination (A–B–C–D) produces effective mulling of spurious responses.

However, it has now been discovered pursuant to the present invention that, in the case of the piezoelectric responses from sand, only a relatively modest 20 dB of attenuation is achieved with this technique, and furthermore because of its asymmetry the sequence tends to produce a large signal off–set, dependent on adjustment of the spectrometer. The reason for these drawbacks is the failure of the PAPS/NPAPS sequence to fulfil exact phase equivalence, that is, as regards phases, the principle that like should be subtracted from like, since the sequence involves three 0° phases but only one 180° phase.

According to the present invention, a revised version of this sequence which does fulfil the phase equivalence principle has been developed. This is shown below:

$$\text{PAPS} \quad \{\overset{A}{\alpha_{0^\circ}}-\tau_1-\overset{B}{\alpha_{180^\circ}}-\tau_2-\}_n$$

$$\text{PAPS} \quad \{\overset{C}{\alpha_{180^\circ}}-\tau_1-\overset{D}{\alpha_{0^\circ}}-\tau_2-\}_n$$

$$\text{NPAPS} \quad \{\overset{E}{\alpha_{0^\circ}}-\tau_1-\overset{F}{\alpha_{0^\circ}}-\tau_2-\}_n$$

$$\text{NPAPS'} \quad \{\overset{G}{\alpha_{180^\circ}}-\tau_1-\overset{H}{\alpha_{180^\circ}}-\tau_2-\}_n$$

and the combination to take is now (A – C – E + G), or, more fully, (A– C – E + G – B + D + H). Such a pulse sequence has been found experimental to produce 33 dB attenuation of the sand response, with no off–set. This performance is comparable with the best achievable by the other variants of the second embodiment.

Performance is further enhanced by carrying out a phase cycled version of the sequence, in which the 0° phases are converted into 90° phases, whilst 180° phases are converted into 270° phases.

Furthermore, in our revised version of this sequence, it is possible to have τ_1 different from τ_2, which would be difficult if not impossible to implement for the method described in U.S. Patent No. 5,365,171 in view of its inherent asymmetry. Having τ_1 different from τ_2 can have advantages in enhancing the signal to noise ratio, as described above in relation to the second variant of the second embodiment.

the relevant nuclear species, and more preferred that τ is less than 0.5, 0.3 or even 0.1 times the free induction decay time, T_2^*. In this regard τ is in fact most advantageously as small as possible.

Thirdly, a condition for the generation of echoes is that the relevant pulse repetition time, which as used herein for some variants may be equal to 2τ, is in any event less than roughly 5 or 10 times T_2^*. For the 3.41 MHz line of RDX, therefore, echoes will be generated if the relevant pulse repetition time is less than roughly 3.5 or 7 ms.

Fourthly, care needs to be exercised in the proper detection of the response signals from echo-generating sequences. At higher values of pulse repetition time (near 5 or 10 times T_2^* or more), most of the magnetization may be concentrated in free-induction-decay type signals which follow or precede a pulse, and so it is this portion of the signal which is preferably detected. At lower values (say, below a pulse repetition time equal to once or twice T_2^*), most of the magnetization eventually becomes concentrated in the echoes or in quasi-stationary steady state type signals, and so a different portion of the signal is preferably detected. At intermediate values of pulse repetition time, both signals may be important, and hence careful adjustment of the receiver phase needs to be effected to ensure optimal signal recovery. If, due to limitations in the testing apparatus being used, the probe ring down time prevents the successful acquisition of free induction decay signals at these intermediate values, then it will be necessary to detect only the echo response signals.

Fifthly, since all the variants of the second embodiment can generate echo-type responses, pulse shaping can be used with frequency and or amplitude modulation, provided that the pulses produced do indeed generate NQR echoes. For instance, pulses shaped as described in United Kingdom Patent Publication No. 2,282,666 (to British Technology Group Limited) may be utilised. The advantage of using such pulses is that a better excitation bandwidth can be achieved relative to single rectangular pulses, particularly when restrictions on the B_1 field to be used or the r.f. transmitter power available necessitates the use of long pulses. This excitation bandwidth is needed when samples at different temperatures are to be examined, as has been already noted in United Kingdom Patent No. 2,255,830 (to British Technology Group Limited). Frequency changes between pulses may also be used to improve the excitation bandwidth.

A further advantage of using appropriately shaped pulses is that the echo

7 ms when the pulse sequences were terminated. It is to be noted that the second, third and further echoes are particularly strong, and it may be advantageous to employ a pulse sequence designed to generate roughly these numbers of echoes.

It is also to be noted from Figure 12 that the technique has removed all traces of pulse breakthrough caused by the ring down of the probe. A particular advantage of removing the pulse break-through is that the effective ring down time of the probe and receiver system can be shortened, so that data acquisition can commence closer to the edge of the relevant pulse.

Reference is now made to Figure 13, which is a plot of echo signal intensity versus, on a logarithmic scale, pulse separation τ. As with the plot of Figure 12, the length of all the pulses was 30 μs. In Figure 13, the first echo was observed following a time of at least 2 ms after the first, initial P1 pulse. The echo signal intensity is observed to vary with the pulse separation τ, reaching a maximum at a value of τ close to 0.3 ms, but, most noticeably, falling sharply at higher values of τ. The free induction decay time, T_2^* for the particular line of RDX being tested was roughly 0.7 ms, and it may be surmised that the sharp fall off above 0.3 ms is caused by inefficient utilisation of the available test time. Further, it can be deduced from Figure 13 that, within limits, the smaller the value of τ the better. Although signal intensity decreases at lower values, more pulse repetitions can be applied to the sample, and more echoes can be observed, in a given time; this can more than compensate for the lowering of the signal intensity.

As regards the variation of signal intensity with flip angle, in a further example, tests were carried out using a two pair pulse sequence akin to that described above, with the length of the three pulses in each individual sequence being varied between 70 and 250 μs, and the pulse separation τ taking values of 1, 0.5 and 0.25. The echo was sampled after n = 1 cycles, with a delay time following the final pulse of 400 μs; the delay time was necessitated by an instrumental restriction, and would normally be very considerably shorter. A pulse length of 250 μs was observed to correspond to a flip angle of $119°_{actual}$, and one of 70 μs was taken to correspond to $33°_{actual}$. The results of these tests are provided in the table below. The final column of the table gives, on the left, the value, in arbitrary units, of the echo intensity for each test, with, on the right, the ratio of the two pairs of echo intensity values for each value of τ.

compensated for by careful manipulation of the received signal, or by the use of excitation at a plurality of discrete frequencies, as taught in International Patent Publication No. WO 92/17794. A further possible solution might be to introduce a small random variation into the pulse repetition time, analogous to the teachings of Freeman and Hill ("Phase and Intensity Anomalies in Fourier Transform NMR", J. Magn. Reson., 4, 366–383 (1971)). This should not alter the strength of the echoes, but only their exact position in time.

Another effect of moving to off-resonant conditions is that the response signal intensity can depend upon whether the frequency offset is positive or negative, more intense signals sometimes being found with a positive frequency offset. This effect may need to be compensated for by skewing the excitation frequency or frequencies to frequencies somewhat lower than the central frequency of the frequency range of interest.

A most important feature of the preferred embodiments of the present invention is their ability to function effectively at low flip angle α. Such ability is important in circumstances where there are limitations on the r.f. power which may be applied to the sample.

The ability to generate echoes at low flip angle is now demonstrated with reference to Figures 14 and 15. The conditions in these two figures are respectively as per the conditions in the first two lines of the preceding table; for Figure 14 the flip angle was $119°_{actual}$ for both the P1 and P2 pulses whilst for Figure 15 the flip angle was only $33°_{actual}$ for both pulses. In each case, the Pulsed Spin Locking sequence described above was used, with n = 1; in other words the echo after the third pulse in the sequence was sampled. In the plots of Figures 14 and 15, each sub-division on the horizontal (frequency) axis represents 0.625 kHZ; the 5.192 MHz line of RDX was excited. It can be seen from the figures that echoes were generated under both conditions of flip angle. Indeed, echoes have been generated pursuant to the present invention at flip angles as low as $10°_{actual}$. They have also been generated with the P1 pulse having a flip angle of $90°_{effective}$, but the P2 pulse having a flip angle less than $90°_{effective}$.

Further experiments pursuant to the present invention have demonstrated that the PSL sequence can produce response signals in a so-called "quasi-stationary" state which persist for long periods even at low values of flip angle.

It should also be stated that all of the pulse sequences mentioned above can

(iii) the signal in response to the equivalent phase alternated sequence of the third variant (the solid line), with the same value of τ;

(iv) the signal in response to the equivalent PAPS/NPAPS pulse sequence described in United States Patent No. 5,365,171 (the triple dashed line), again with the same value of τ.

Signals (ii) to (iv) were obtained at the end of their respective sequences. With a pulse repetition time of 1.5 ms and a dead time of 0.2 ms, during the pulse sequence signal acquisition actually only occurs over the first 1.3 ms of the signal shown in Figure 18.

Clearly the plain unattenuated sand signal (i) predominates; of the sequences specifically designed to attenuate the sand signal, the second and third variants ((ii) and (iii)) perform the best, whilst the PAPS/NPAPS sequence (iv) performs rather worse.

Most of the same information is also shown in Figure 19, but with the signal intensity being shown to a larger scale (the response to a single pulse not being shown). The same signals are denoted by the same line types. Also shown in Figure 19 is the signal corresponding to signal (ii) above, but using the explosive RDX instead of sand (the full black symbols).

It can be seen that the results using the second and third variants are roughly equivalent (representing a roughly –33 dB attenuation of the sand signal) whereas the result using the PAPS/NPAPS sequence is considerably worse (representing only a roughly –20 dB attenuation). In comparison the equivalent signal obtained from the explosive RDX in the absence of sand is less intense than the sand signals obtained using the PAPS/NPAPS sequences and signal (i), suggesting that for the particular experimental circumstances used neither a non–phase–cycled sequence nor the PAPS/NPAPS sequence would have detected the RDX. Whilst in general results using the second and third variants have been found to be roughly comparable, often one variant or the other has been found to be marginally more effective for a specific condition. This is thought to be due to the different phases which the two variants employ at various times.

THIRD EMBODIMENT – HYBRID

A third preferred embodiment of the present invention is effectively a hybrid of the first variants of the previous two embodiments, in that each individual pulse

It will be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.

Each feature disclosed in the description, and (where appropriate) the claims and drawings may be provided independently or in any appropriate combination.

second pulses being preferably less than the length of the second pulse, the second pulse at least partially locking the magnetization generated by the first pulse.

7. A method of nuclear quadrupole resonance testing a sample containing quadrupolar nuclei, comprising:

applying a pulse sequence to the sample to excite nuclear quadrupole resonance, the pulse sequence comprising at least a first pulse and a second pulse, the time between the first and second pulses being less than the length of the second pulse, the second pulse at least partially locking the magnetization generated by the first pulse; and

detecting response signals.

8. A method according to Claim 6 or 7 wherein the length of the second pulse is less than 5 times the value of $T_{1\rho}$ of said quadrupolar nuclei.

9. A method according to any of Claims 6 to 8 wherein the second pulse comprises two phase alternated elements.

10. A method according to Claim 9 wherein the second pulse includes a third element having a phase different from said two phase alternated elements.

11. A method according to any of Claims 6 to 10 wherein the length of the second pulse is less than, preferably no more than 75% of, more preferably no more than 50% of, the length of the first pulse.

12. A method according to Claim 11 wherein the phase of the second pulse is in quadrature with that of the first pulse.

13. A method according to any one of Claims 6 to 12 including a third pulse at least partially locking the magnetization generated by the first and second pulses, and preferably being of phase intermediate that of the first and second pulses.

14. A method according to any of Claims 6 to 13 wherein at least one of the first and second pulses comprises a plurality of elements of different phase.

15. A method according to any of Claims 6 to 14 wherein the phases of the first and second pulses are arranged so as to provide together excitation peaks at at least two different frequencies.

16. A method according to any of Claims 1 to 5 wherein the pulse sequence comprises at least one pulsed spin locking pulse sequence.

17. A method according to any of Claims 1 to 5 wherein the pulse sequence is an echo generating sequence comprising pulses having only relative phases 0° and 180°, or 0°, 90°, 180° and 270°.

of pulses is of a first type, and the pulse sequence further comprises at least one further second type pair of pulses, corresponding to the or each first type pair, but having cycled phases.

26. Apparatus according to Claim 23, 24 or 25 wherein the pulse sequence comprises first and second individual pulse sequences, each including an initial pulse followed, in the case of the first individual pulse sequence, by one respective member pulse of the or each pair, and, in the case of the second individual sequence, by the other respective member pulse of the or each pair, the initial pulses of the first and second individual sequences differing as to phase.

27. A pulse sequence for exciting nuclear quadrupole resonance in a sample comprising a first type substance containing quadrupolar nuclei and a second type substance which may give rise to spurious signals which interfere with response signals from the quadrupolar nuclei, comprising at least one pair of pulses, the pulse sequence being such that the respective spurious signals following the two member pulses of the pair can be at least partially cancelled without the corresponding true quadrupole resonance signals being completely cancelled, and, for the or each such pair, the two member pulses being of like phase.

28. A method of nuclear quadrupole resonance testing a sample, substantially as herein described.

29. Apparatus for nuclear quadrupole resonance testing a sample, substantially as herein described with reference to and as illustrated in any of Figures 1 to 19 of the accompanying drawings.

30. A pulse sequence for exciting nuclear resonance, substantially as herein described with reference to and as illustrated in any of Figures 1 to 19 of the accompanying drawings.

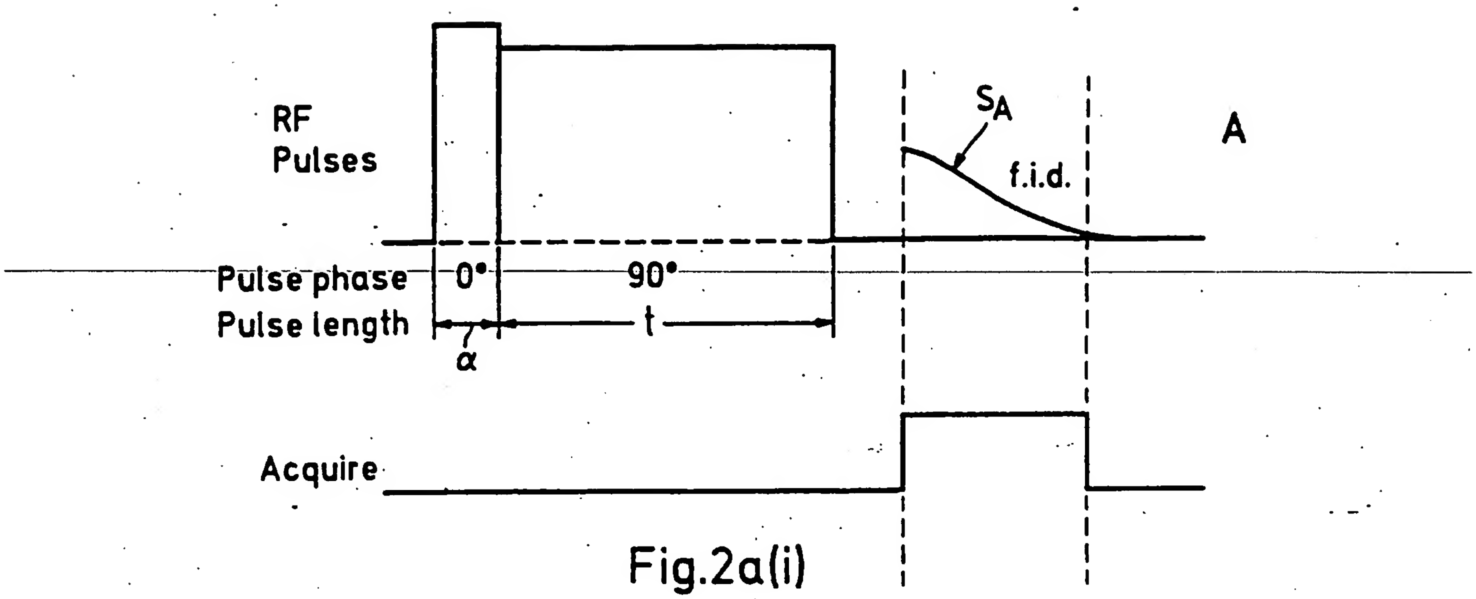

Fig.2a(i)

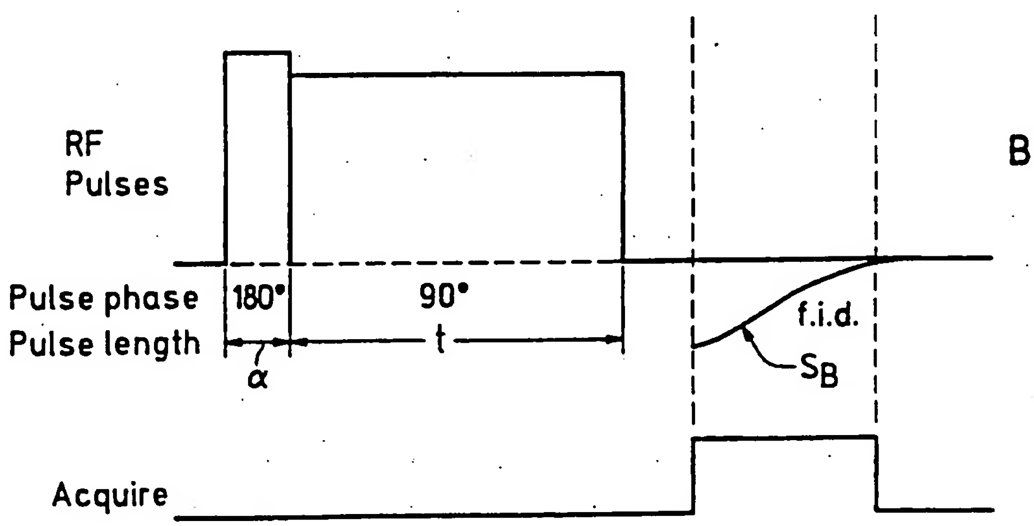

Fig.2a(ii)

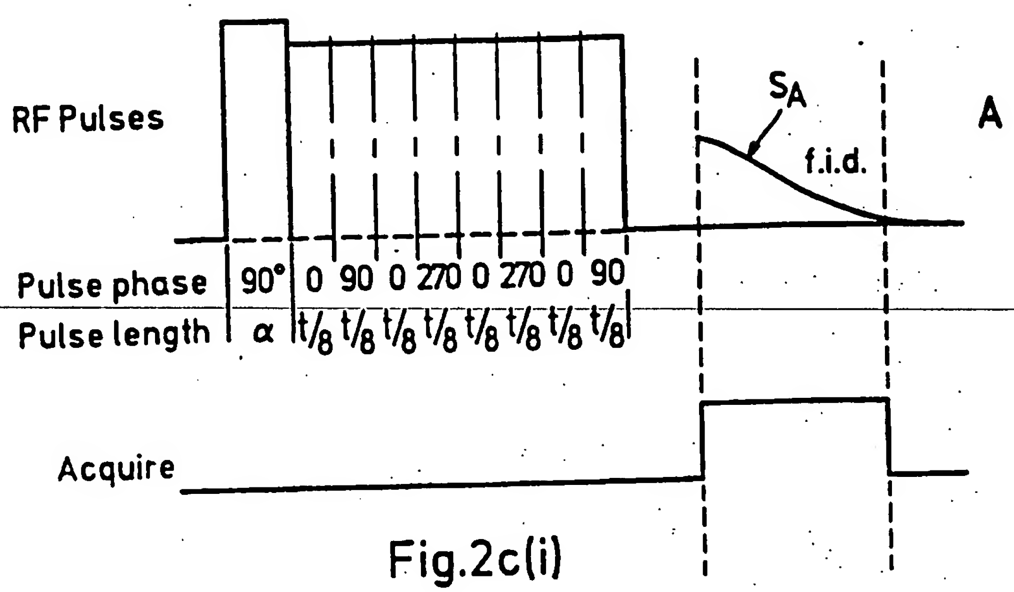

Fig.2c(i)

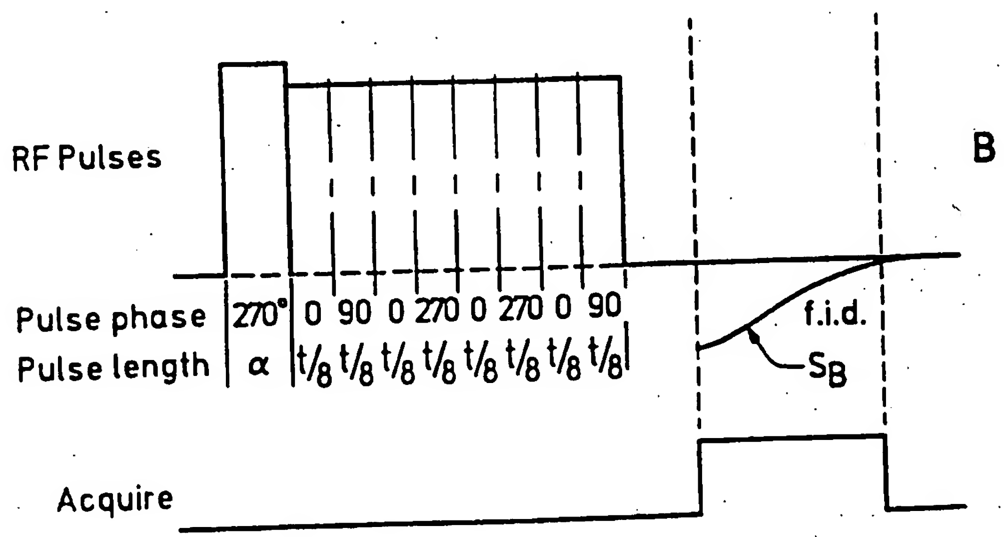

Fig.2c(ii)

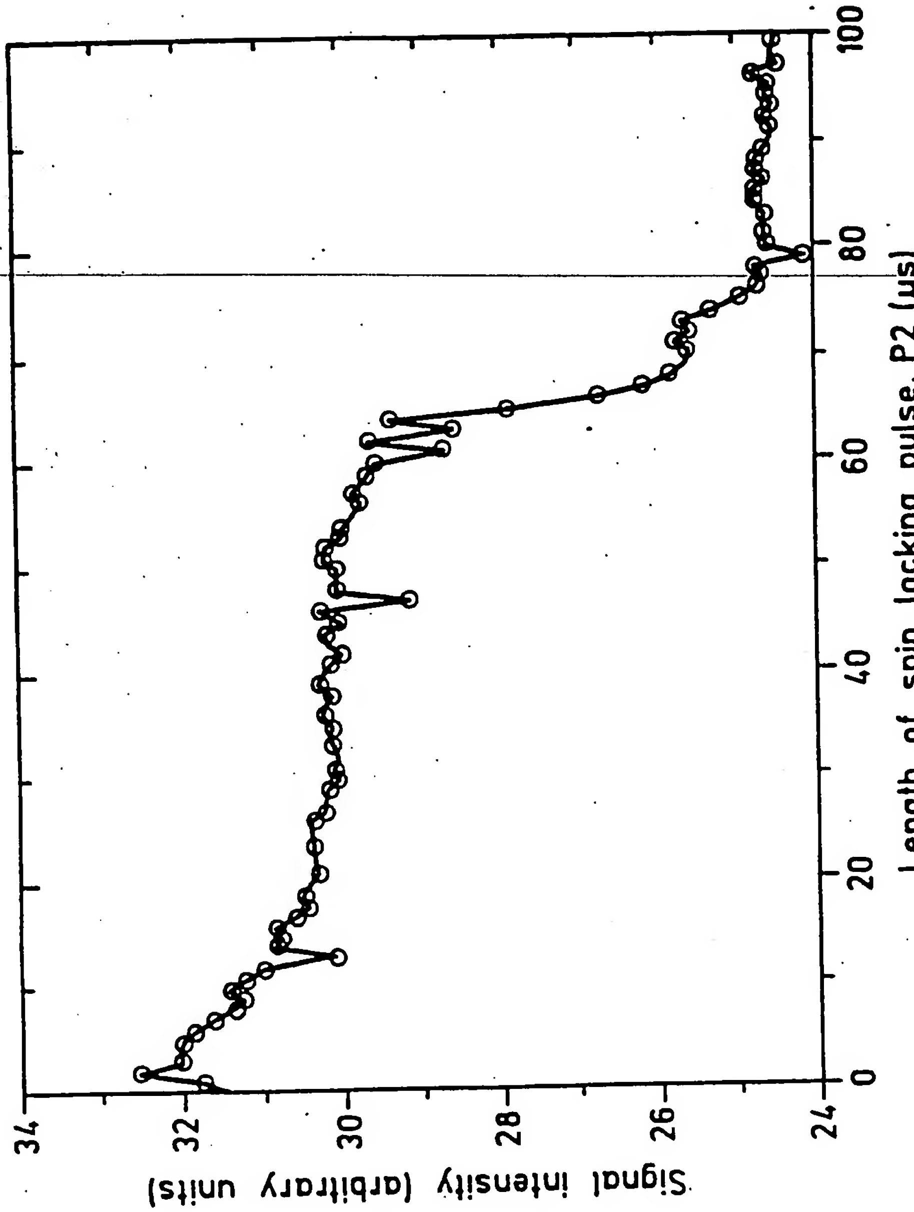
Signal intensity (arbitrary units)
34
32
30
28
26
24
0
20
40
60
80
100
Length of spin locking pulse, P2 (µs)

Fig.3

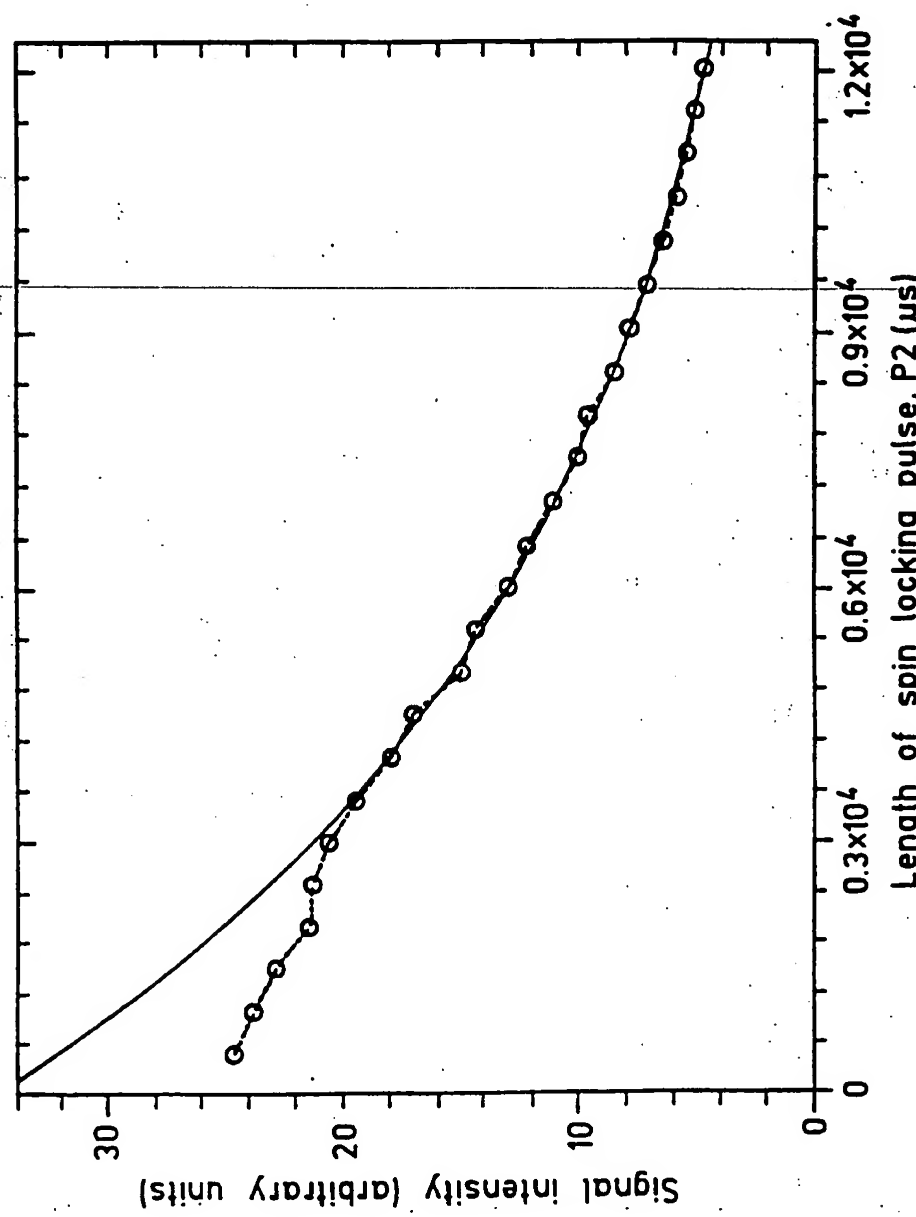
Signal intensity (arbitrary units)
30
20
10
0
Length of spin locking pulse, P2 (μs)
0
0.3x10⁴
0.6x10⁴
0.9x10⁴
1.2x10⁴

Fig.5

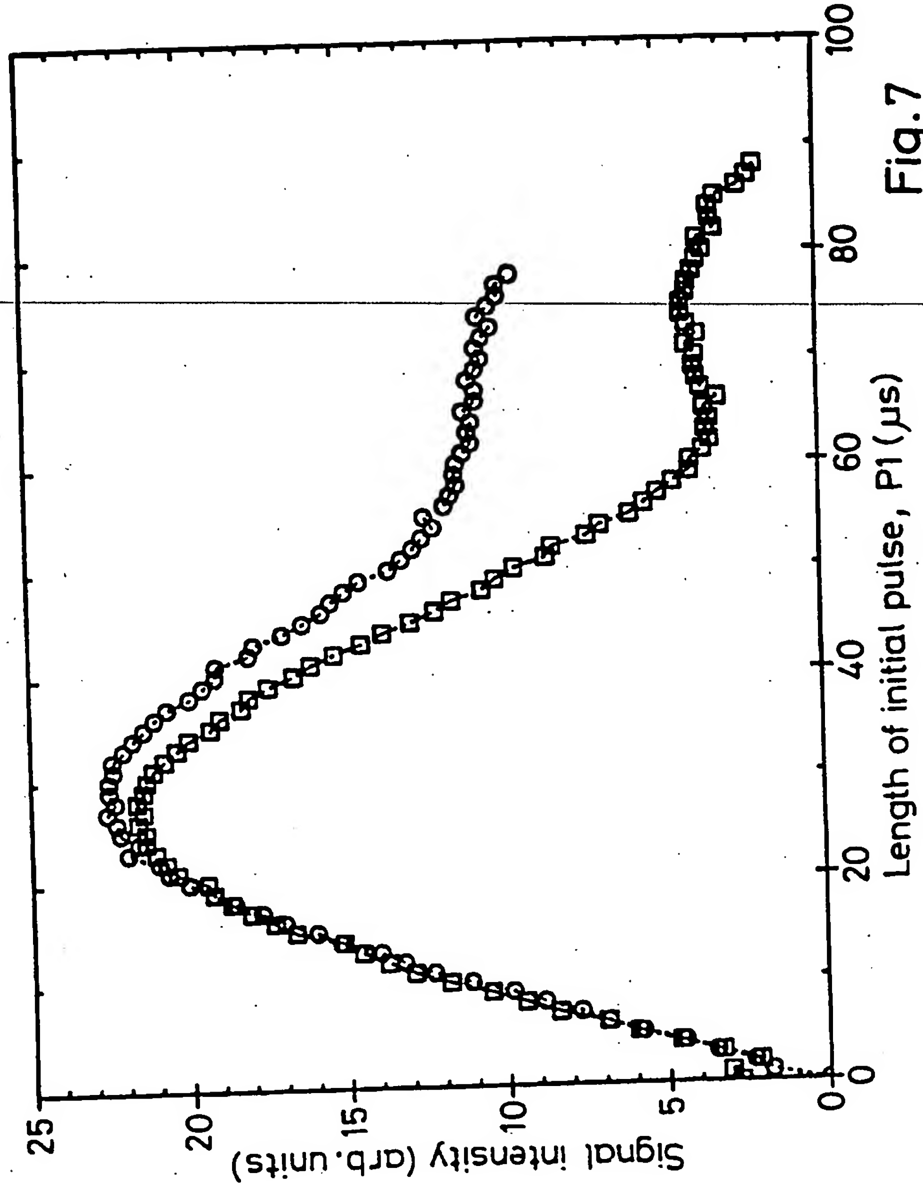
Signal intensity (arb. units)
0
5
10
15
20
25
Length of initial pulse, P1 (μs)
0
20
40
60
80
100

Fig.7

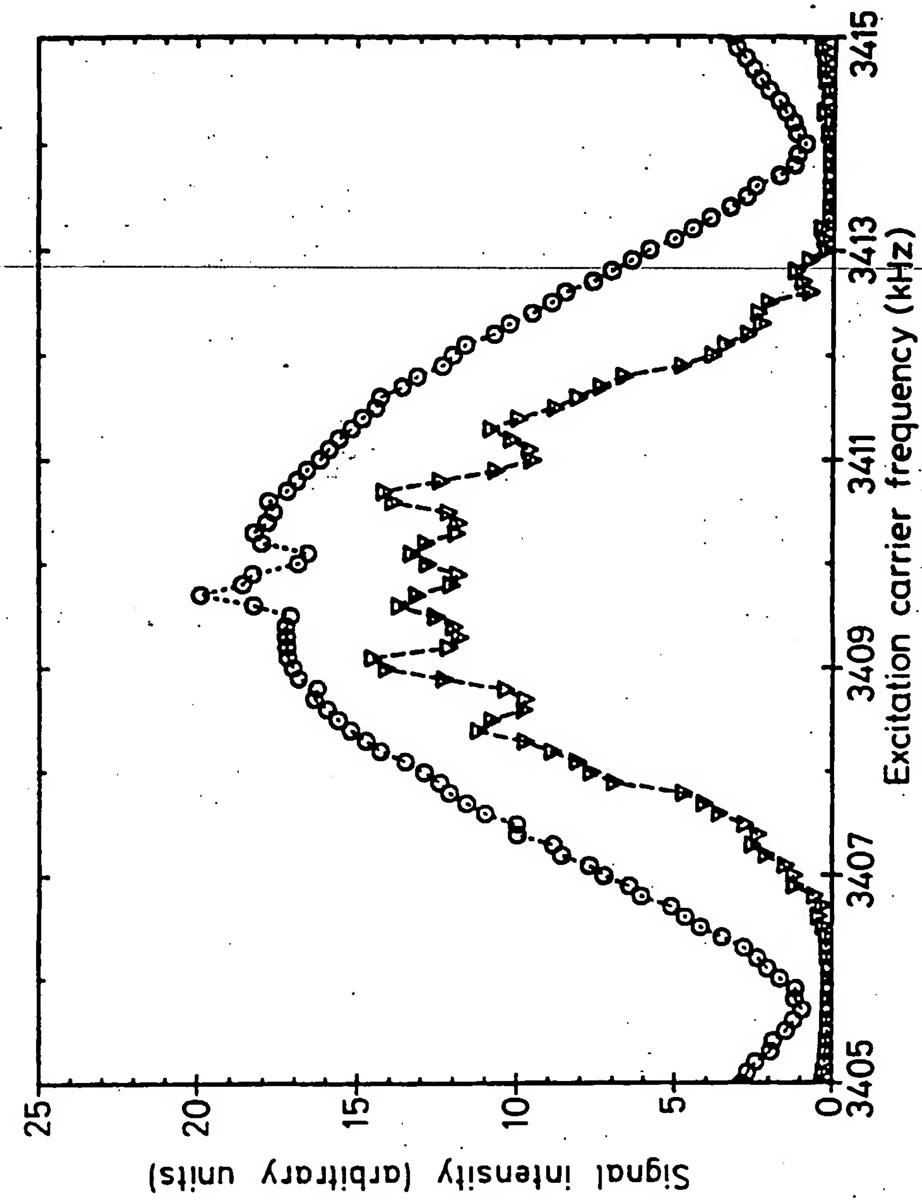
Signal intensity (arbitrary units)
25
20
15
10
5
0
3405
3407
3409
3411
3413
3415
Excitation carrier frequency (kHz)

Fig.9

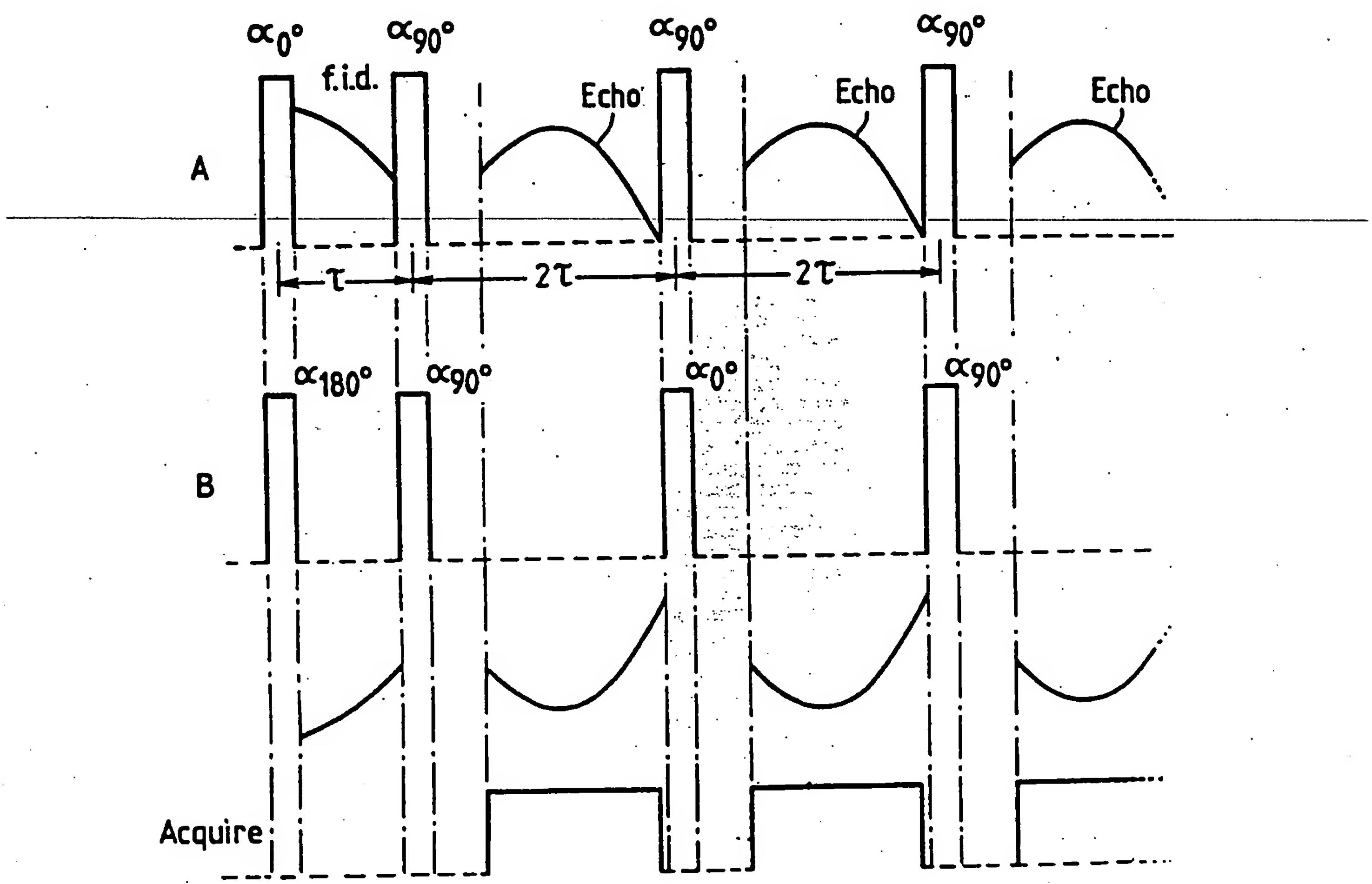
$\alpha_{0°}$
f.i.d.
$\alpha_{90°}$
Echo
$\alpha_{90°}$
Echo
$\alpha_{90°}$
Echo
A
τ
2τ
2τ
$\alpha_{180°}$
$\alpha_{90°}$
$\alpha_{0°}$
$\alpha_{90°}$
B
Acquire

Fig. 11

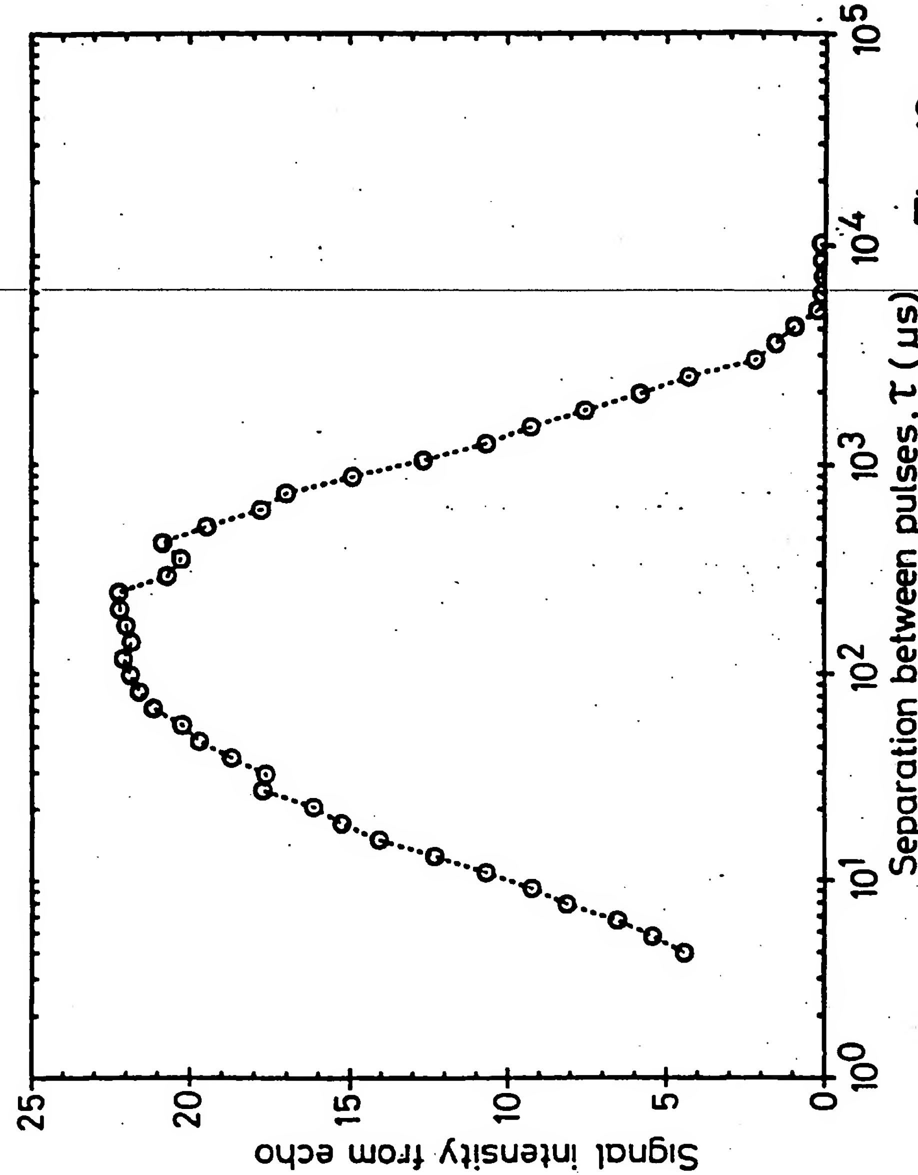
Signal intensity from echo
25
20
15
10
5
0
10^0
10^1
10^2
10^3
10^4
10^5
Separation between pulses, τ (μs)

Fig. 13

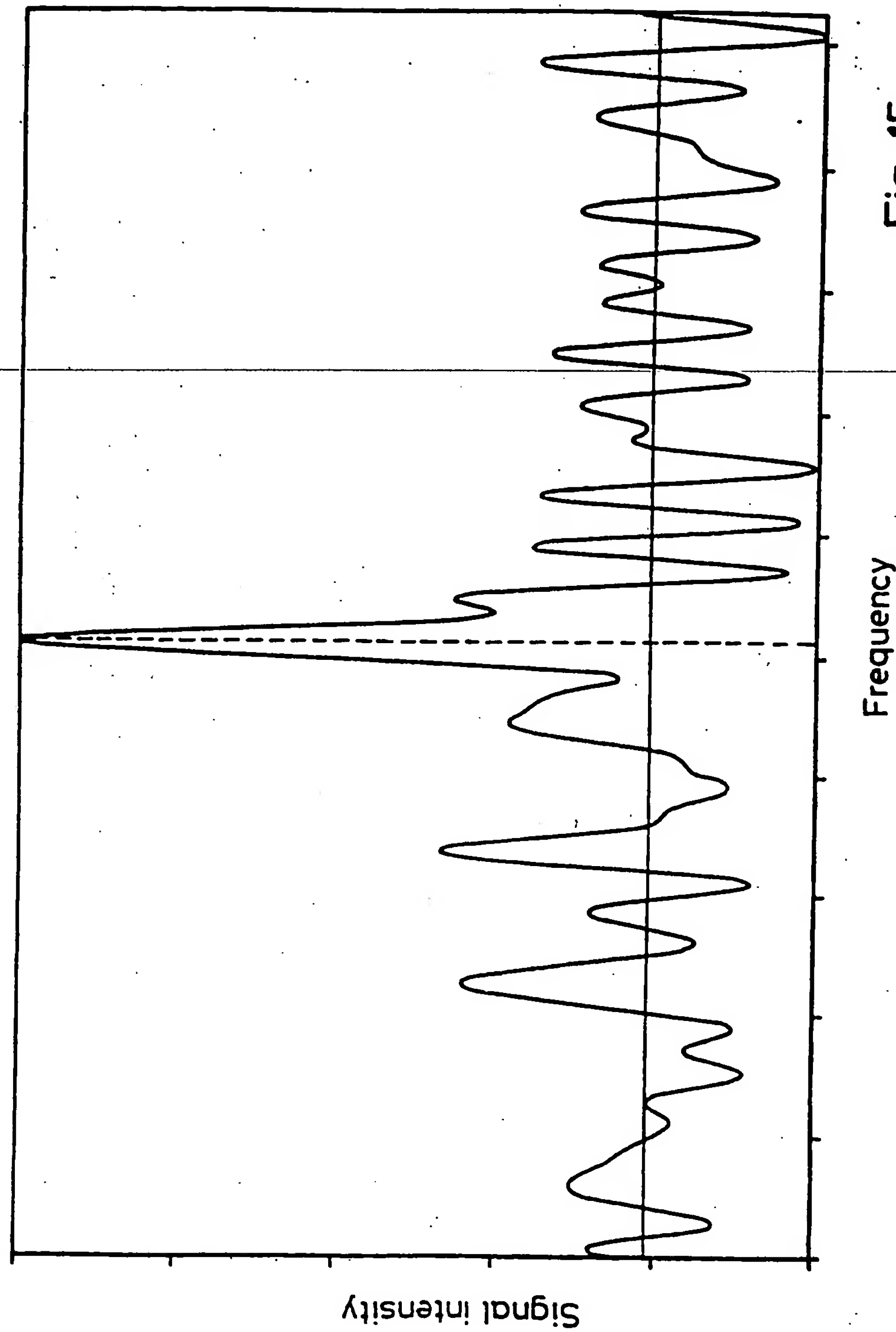

Fig. 15

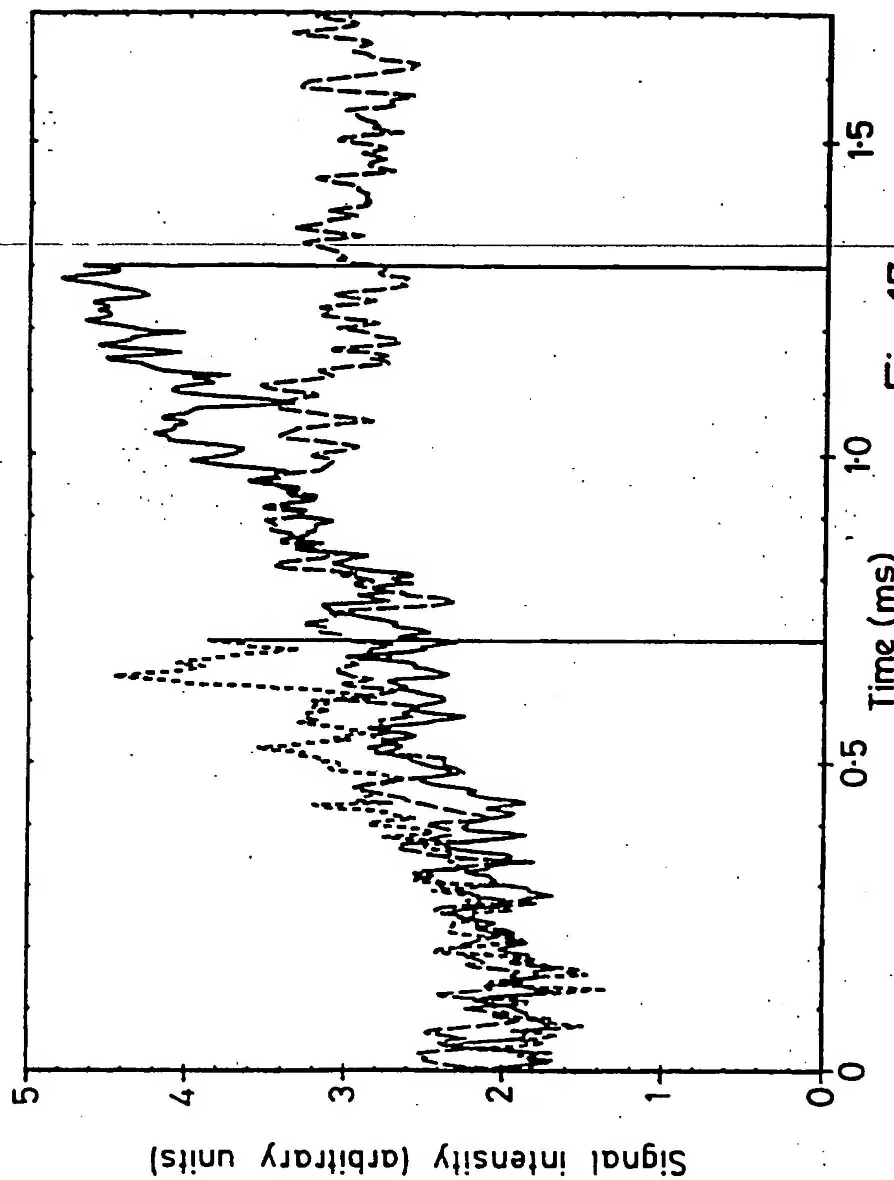

Fig.17

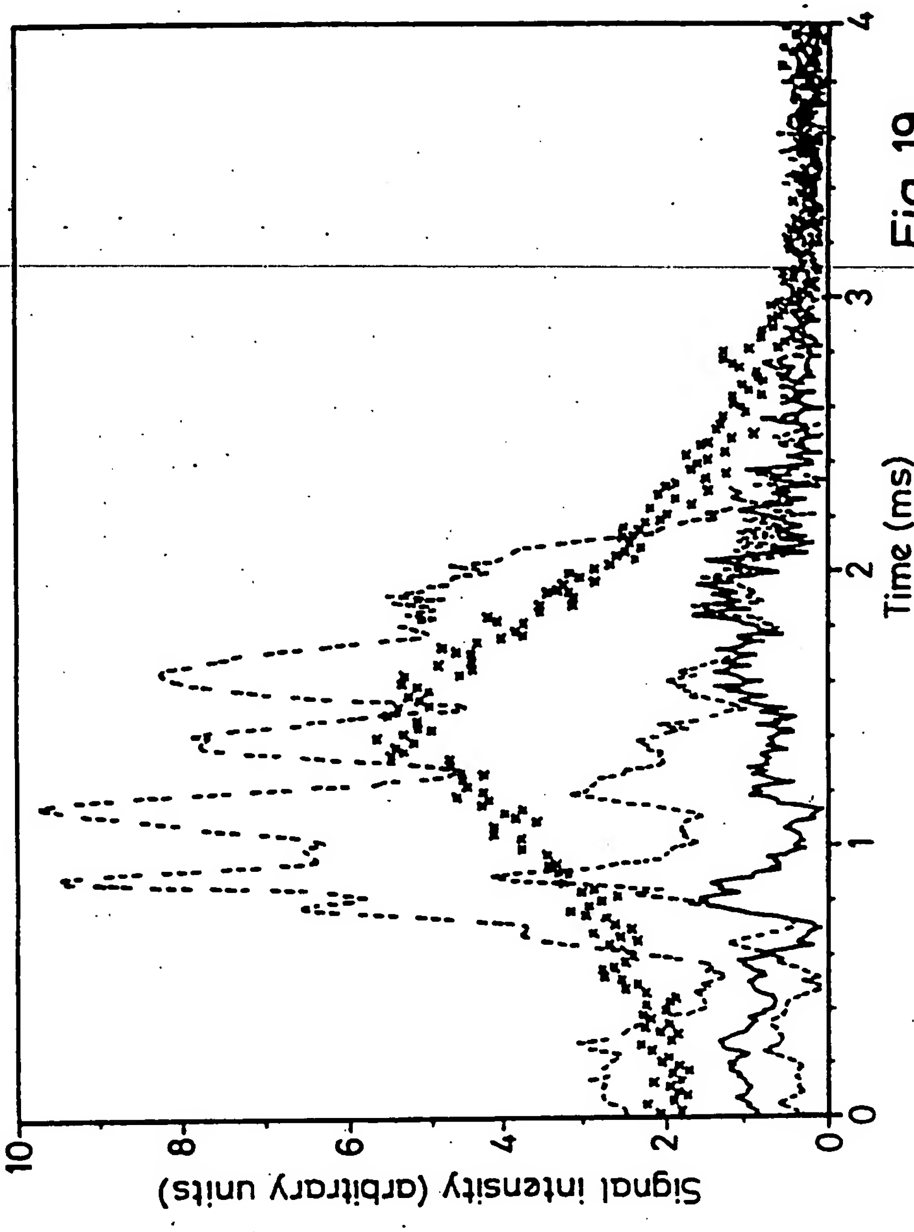

Fig. 19